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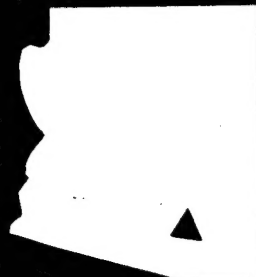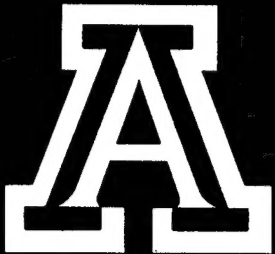
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**Synthesis and Processing of Organically
Modified Oxides for Optical
and Electrical Applications**

Submitted by

Professor Donald R. Uhlmann
Department of Materials Science
and Engineering
College of Engineering and Mines
The University of Arizona
Tucson, AZ 85721

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ENGINEERING EXPERIMENT STATION
COLLEGE OF ENGINEERING AND MINES
THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

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Professor Donald R. Uhlmann

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Department of Materials Science and Engineering
College of Engineering and Mines
The University of Arizona
Tucson, AZ 85721

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This final report summarizes the work performed on the AASERT-sponsored program dealing with "Gradient Index Devices from Polycerams". The purpose of this project was to develop a new processing method to create large dimension (bulk) inorganic/organic Polyceram materials for optical lens applications. During this project, prototype monolithic and gradient refractive index (GRIN) optical lens materials were successfully formed by chemically synthesizing Polyceram precursor solutions and depositing tailored multiple coatings in order to form self-supporting materials. Determination and tailoring of the appropriate Polyceram chemistry as well as coating, deposition, and drying parameters resulted in the ability to freestanding and highly transparent optical materials with desired gradients in refractive index.

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FINAL REPORT

ON

AASERT GRANT F49620-92-J-0308

ON

GRADIENT INDEX DEVICES FROM POLYCERAMS

SUBMITTED BY

UNIVERSITY OF ARIZONA

Donald R. Uhlmann
Principal Investigator
December 20, 1995

I. PERSONNEL AND RELATION TO PARENT GRANT

The parent AFOSR grants to which the AASERT support is linked are:

F49620-91-C-0033 (through 7/31/94)

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During the 12 month period prior to the AASert award, the funding of the parent grant was $165,000. This suppported one postdoctoral associate and two graduate students.

During the 12 month period after the AASERT award, the funding of the parent grant was $171,999. This supported three graduate students and two quarter-time undergraduate students.

The amount of funding provided by the AASERT grant during the 12 month period after its award was $15,169. This supported one graduate student.

The graduate student supported by the AASERT grant, Mr. Robert Wade, is a US citizen. He received his undergraduate degree from the University of Missouri-Rolla before coming to the University of Arizona for his graduate studies.

II. OVERVIEW

This final report summarizes the work performed on the AASERT-sponsored program dealing with "Gradient Index Devices from Polycerams". This purpose of this project was to develop a new processing methods to create large dimension (bulk) inorganic/organic Polyceram materials for optical lens applications. During this project, prototype monolithic and gradient refractive index (GRIN) optical lens materials were successfully formed by chemically synthesizing Polyceram precursor solutions and depositing tailored multiple coatings in order to form self-supporting materials. Determination and tailoring of the appropriate Polyceram chemistry as well as coating, deposition, and drying parameters resulted in the ability to form freestanding and highly transparent optical materials with desired gradients in refractive index.

Significant results from this research include the ability to form very thick (> 10 micron) sol-gel derived coating layers; the ability to over wide ranges tailor the refractive indices and dispersion of the Polyceram coatings; and the ability to form thick (large-dimension) optical materials containing continuous changes in the refractive index. This latter ability has for the first time allowed the opportunity for developing large diameter GRIN lenses with superior imaging characteristics than available with traditional lenses having a single refractive index and larger diameters than available with state-of-the-art glass GRIN lenses. The expected applications for Polyceram-based GRIN lenses are numerous. These lenses can improve optical communications and computing, copiers, night-vision goggles, microscopes, binoculars, telescopes, and film and video cameras. Further, many additional optical applications using Polycerams GRIN lenses are expected to be developed during the coming months.

The highly encouraging results obtained to date have lead to two patent disclosures being prepared on the concept and preferred embodiments.

TABLE OF CONTENTS

III. PROJECT OBJECTIVES

The overall objective of this research project was to develop a process for creating monolithic and gradient refractive index (GRIN) optical devices derived from inorganic/organic composite Polyceram materials developed under the AFOSR parent grant. The specific objectives of the current research included:

1) Tailoring Polyceram chemistry to form thick (>1 micron) coating layers which are used to form bulk monolithic materials;

2) Optimizing the drying of Polyceram coatings such that a bulk optical material can be formed by a process of repetitive coating and drying;

3) Determining conditions under which two Polyceram solutions of widely differing refractive index can be combined without phase separation, precipitation, or other deleterious effects, in order to tailor the refractive indices of Polyceram coating layers;

4) Developing a computer-controlled system to provide with precision Polyceram layers with programmed variations in refractive index as a function of the number of the layer deposited; and

5) Creating prototype optical GRIN devices by serially depositing thick Polyceram layers while varying the refractive index of each layer, thereby forming substantially continuous refractive index gradients across large diameter rods.

IV. PROJECT SUMMARY

This 3-year research project was organized and executed in the same order as the above project objectives. Briefly, highlights of the research project included:

1992-93 (Year 1):

- Selection of two Polyceram systems for investigation: TiO_2-SiO_2-MPEOU and TiO_2-SiO_2 PDMS.
- Formation of crack-free monolithic Polyceram cylinders and plates by casting;
- Development of suitable Polyceram solutions for the formation of crack-free, thick coatings by a dip coating process;
- Initial development of a computer-controlled dip coating machine;
- First formation of prototype GRIN cylinders; and
- Initial attempts at sectioning and polishing of bulk Polyceram samples.

1993-94 (Year 2):

- Variation of the composition, and particularly of the oxide/polymer ratio, to improve coating and drying conditions;
- Improvement of the Polyceram dip coating machine to include a computer controlled drying chamber to decrease the drying time of each layer, and enclosure of the Polyceram solution bath to prevent solvent evaporation;
- Tailoring of the Polyceram solution chemistry to form high refractive index fibers, which serve as the initial surface (core) for cylindrical lens formation;
- Development of improved sectioning and polishing methods; and
- Formation of improved radial GRIN cylinders.

1994-95 (Year 3:)

- Modification of the Polyceram dip coating machine to minimize vibrations associated with the motor used to translate the sample between the coating and drying stations;

- Exploration of improved solvents for the Polyceram solutions;

- Use of vacuum oven and microwave oven drying to improve the long-term mechanical and optical stability of the bulk Polyceram materials.

- Optimization of variations in coating solution with layer number to improve refractive index profile; and

- Demonstration of prototype radial-GRIN lenses with large diameters and technologically-attractive optical properties.

V. BACKGROUND

1. Polycerams

In the past several years, a unique new class of nanocomposite materials called Polycerams have been created by intimately combining ceramic and polymer materials on a nanoscale level during wet chemical synthesis of the materials [1, 2]. The formation of homogenous Polycerams from disparate polymer and ceramic precursors has resulted in materials with novel optical, electronic, mechanical, and physical properties, due in part to the synergistic effects of the constituents of the materials, which can be tailored to produce novel nonocomposites. One of the most striking features of Polycerams is the high optical transparency observed in these materials, which is comparable to or exceeds that of oxide glasses [3]. These new materials are synthesized at low temperatures by similar wet chemical processing techniques as those used to produce sol-gel derived ceramic materials by the addition of functionalized polymers into the inorganic sol-gel precursor solutions prior to gelation of the Polyceram material. After gelation, the remaining solvent and water are removed by appropriate drying/curing either at room temperature or elevated temperatures, resulting in a highly transparent, virtually pore-free material. For a thorough discussion of sol-gel chemistry and processing, extensive reviews are available [4, e.g.].

The flexibility of the polymer component of the Polyceram allows significant relaxation and rearrangement to occur during drying of the gel, typically resulting in fully dense films and bulk materials. This is in sharp contrast to the deleterious cracking, shrinkage, and warpage of most bulk sol-gel derived ceramic materials. Further, the low temperature synthesis of Polyceram materials allows the direct incorporation of many additional materials, including NLO and laser dyes, quantum dot constituents, and biological components [5-7]. Significant tailoring of the Polyceram structure and properties may be

easily achieved by varying the types and amounts of polymer and ceramic as well as the processing and drying conditions [8]. For example, polymer-rich Polycerams typically display rubber-elastic behavior [9], whereas ceramic-rich Polycerams are usually rigid and tough [8].

In order to form a single phase, highly transparent material from the disparate polymer and ceramic components, the polymer materials are typically modified to contain one or more functional groups, including hydroxyl (-OH) and trialkoxysilyl ($-Si-(OR)_3$) groups [2, 3, 10]. The modified polymer may then directly participate in the sol-gel hydrolysis and condensation reactions, forming one or more bonds between an individual polymer molecule and the inorganic oxide network. A wide gamut of polymers have been incorporated into Polycerams, ranging from soft, rubbery polydimethylsiloxanes/silicones (PDMS) to stiffer polyethylene oxide, polybutadiene, and polyethyleneimine [10] and polytetramethylene oxide [11]. The types and concentrations of the ceramic and polymer constituents which may be incorporated into Polycerams are practically unlimited.

2. GRIN Lenses, Materials, and Processing

The refractive index (n) of a homogenous material represents the ratio of the velocity of light in a vacuum relative to the velocity of light within the material. The very low densities of air and other gases hardly slow the velocity of light, and thus have nearly the same refractive index as a vacuum. However, homogenous liquids, glasses, polymers, and ceramic single crystals have a much higher refractive index than air, corresponding to a significant reduction in the velocity of light transmission through these materials. If a light ray encounters a change in the refractive index, the direction of light propagation is altered due to refraction, as related through Snell's law:

$$\sin \theta_t = (n_i / n_t) \sin \theta_i$$

where θ_t is the angle of transmission, θ_I the angle of incidence, n_I and n_t the refractive indices of the incident and transmission regions, respectively.

Traditional curved lenses used in most optical applications are formed of transparent, homogenous (single refractive index) materials including oxide glasses and polymers. The desired focusing or other processing effect is achieved only by the refraction of light at the entrance and exit lens surfaces. Typically, two to five curved lenses must be used together to minimize the aberrations caused by each individual lens. If the refractive index of a lens is not homogenous, then light is refracted within the lens in addition to the surfaces.

In contrast, for a lens whose refractive index is continuously changing to provide a gradient index (GRIN) structure, light passing through the material is continuously refracted along a curved path within the material proportional to the magnitude of the refractive index change. This ability of bending light allows GRIN lenses to be formed with a larger field of view and without distortions such as chromatic or spherical aberration inherent in curved lenses.

To date, GRIN lenses have been limited in their imaging ability, primarily due to the expense and the limited range of materials in which a suitable refractive index gradient can be formed. All GRIN lenses have five fundamental requirements which must be satisfied to be suitable for low distortion imaging:

1) a significantly large variation in the refractive index (Δn);
2) a suitable depth of the gradient (e.g., the radius of a cylindrical lens);
3) an appropriate refractive index distribution (profile) to form a desired imaging condition (e.g., magnifying, reducing, or collimating lens);
4) a minimal deviation from the desired gradient profile to avoid lens aberrations;

5) a practical, timely, and cost-effective method of forming the gradient in refractive index.

The magnitude of Δn is the most critical GRIN lens variable, for it controls the numerical aperture, field of view, lens power, radiometric speed (light gathering ability), and required GRIN lens thickness. An increase in Δn allows the lens to gather a larger image while allowing the thickness of the lens to be reduced. The radiometric speed is proportional to the square of Δn.

The most common types of GRIN lenses are cylindrical in shape and possess a radial gradient perpendicular to the cylindrical axis, as shown schematically in Figure 1. These lenses characteristically possess flat surfaces and contain a parabolic-type gradient profile to process images similar to convex or concave curved lenses—but with less distortion. The most common radial GRIN lens performs as a low distortion convex lens, with the refractive index profile typically following a parabolic profile, as:

$$n(r) = N_{00} + N_{10} \, r^2$$

where N_{00} is the refractive index of the center at the lens, N_{10} is a quadratic focussing coefficient (a constant), and r is the radial position in the lens. During every quarter of the lens pitch, the radial GRIN lens either focuses light rays to a point or collimates the light into parallel rays, as shown schematically in Figure 2. Further, by increasing or decreasing the lens pitch (thickness), the lens can magnify or reduce an image, as demonstrated schematically in Figure 3.

There are a number of special optical advantages of using a radial GRIN lens over traditional lenses, including greater optical power, a larger field of view, and the elimination

of common curved lens aberrations such as Petzval field curvature and paraxial color. Depending upon the specific application, the radial GRIN profile can be tailored to eliminate different aberrations or create novel imaging conditions which cannot be physically or economically formed with curved lenses. For example, other profiles include a concave-type reducing lens [12] or a "W"-type profile lens for low modal dispersion in optical signal devices [13]. Radial GRIN lenses with diameters greater than 1 cm are desirable for numerous applications including cameras, binoculars, and eyeglasses.

An axial GRIN lens contains planes of constant refractive index normal to the optic axis. This type of lens can be used to correct for spherical aberration inherent in traditional camera and binocular designs [14, 15]. A linear gradient is commonly used in the axial lens. To date, the development of axial GRIN lenses has been limited to materials with a Δn of <0.05 and limited gradient depth of <4 mm [16]. The GRIN lens imaging properties have been enhanced by curving the front and back surfaces of the lens to gain additional imaging power. However, with the development of lenses with larger linear Δn, it should be possible to use axial lenses with flat surfaces in optical systems. Spherical GRIN lenses contain a symmetrical gradient in 3-D about a central point. Small spherical or hemispherical lenses have been developed for use in photocopying systems, microoptics, and integrated optics applications [17]. However, these lenses are limited to a small size (1-2 mm).

Combinations of one- and two-dimensional gradients have recently been formed by the fusion of multiple (~10) layers of glass powders or fused plates of different refractive index, achieving overall Δn values approaching 0.5 for depths up to 10 mm for nearly linear gradients up to 5 mm for nearly parabolic gradients. However, their use is primarily for gathering incoherent light for photovoltaic (solar cell) applications. Use as an imaging GRIN lens has not been reported, and contamination from container materials is considerable [18,19].

Refractive index gradients are typically formed by the chemical modification of previously melted oxide or wet-chemically derived (sol-gel) glasses, or in polymers by directional copolymerization in polymeric systems. Candidate materials are selected for high optical transparency, stability, and the ability to be processed with other materials of different refractive index without phase separation or other deleterious reactions.

The most common preparation method for forming fused glass radial GRIN lenses is by an ion exchange process, where cations of the glass are exchanged to modify the refractive index [20,21]. Typical exchange pairs include thallium for potassium (technologically the most important), silver for sodium, and lithium for sodium. Initially, a high-index base glass blank is formed which is then ion exchanged with one or more ions which decrease the refractive index. The ion exchange is carried out using a highly corrosive molten salt bath at high temperatures. A disadvantage of the ion exchange technique is the likelihood of fracture due to the stress resulting from the gradient in ion sizes within the glass. A number of variations of the basic ion exchange process have been developed to speed up the slow diffusion process, including field-assisted ion exchange, double ion exchange, phase separation/leaching, and ion stuffing. For all these techniques, the very slow diffusion and substitution of ions inherently limits the size of glass GRIN lenses to less than 5 mm in diameter. Further, due to the high temperatures commonly used to enhance diffusion, it has proven difficult to form the desired refractive index profile; and the time and energy requirements to form such a gradient are formidable. For a complete review of glass GRIN fabrication techniques, see references [22].

During the past ten years, sol-gel processing has been increasingly used to form radial GRIN glass lenses. The typical process initially reacts suitable oxide precursors in solution, thereby creating a porous, wet gel. The gels typically contain SiO_2 as the network backbone and one or more additional components such as the oxides of Ge, Ti, Zr, Na, or Al.

Analogous to the ion exchange process in fused oxide glasses, the gel-derived glasses are then subsequently immersed in an alcohol/salt or alcohol/alkoxide solution to modify the refractive index. The highly mobile sol-gel structure allows very rapid diffusion (approximately two orders of magnitude faster than fused glass) and allows a larger variety of dopants to be incorporated into the glass. However, the fragility of the gel and large shrinkage of the sol-gel material during drying often result in fracture during processing. A comprehensive review of sol-gel derived GRIN materials is given in references 22 and 23.

With a low-index salt solution, the salt ions diffuse into the gel and replace the higher index ions, analogous to the ion exchange of fused glasses [23]. Common salt exchange pairs include potassium for Tl, Cs, Rb, or Pb. Unfortunately, during the drying of the gel, the salt cations are mobile and continue to migrate and reduce the magnitude of the refractive index gradient. GRIN lenses up to 13.5 mm in diameter with Δn values of 0.05 have been formed [24,25]. In order to mitigate the undesirable diffusion of the low-index ions during gel drying, the use of low-index alkoxide solutions have become the preferred method for creating sol-gel GRIN materials [26]. The low-index alkoxides and their hydrolysis/condensation products are initially present in the primary gel composition and are subsequently leached out by placing the gel in an acidified water or acetone solution. The low-index constituents which remain in the gel condense and become incorporated in the gel network during drying. The largest lens produced by the alkoxide-leaching technique is reported as about 6 mm in diameter with a Δn of 0.07 [27].

The formation of polymer radial GRIN materials is typically achieved by preferential copolymerization of two or more homopolymer solutions of different refractive indices. The most common technique is a two-step copolymerization process [28]. A partially polymerized rod of high refractive index polymer is formed and is immersed in a low index monomer solution to allow diffusion to occur inward from the rod surface. The system is heated to polymerize fully both materials, forming a parabolic gradient over a radius of up

to 5 mm. A second process of forming polymer GRIN devices is by photo copolymerization [29]. The basis of this technique is the simultaneous gelation of two or more photo active monomers inside of a glass tube using a UV light source and suitable light-activated initiator. Initially, the more reactive monomer polymerizes at the surface of the glass tube. Eventual depletion of the reactive monomer leads to formation of a radial gradient. Unfortunately, the large thermal expansion and poor ultraviolet radiation resistance of the polymer materials formed by both techniques has limited further development of polymer GRIN materials.

As described above, there is a lack of materials and technology to produce economically GRIN lenses with large enough Δn and lens size for many commercial applications. The present research program seeks to overcome the above drawbacks to forming large diameter GRIN lenses by using newly developed optical Polyceram technology.

VI. YEAR 1 RESEARCH (1992-1993)

Polyceram Chemistry

Two areas were initially targeted for the development of bulk Polyceram GRIN materials. First, the chemistry and processing to form highly transparent Polyceram thin films were adapted to form bulk materials. Polyceram materials, one with a high refractive index (2:1 molar ratio of titania-silica) and the other with a low refractive index (pure-silica), were selected based upon their relative ease of fabrication and high optical transparency. Based upon results obtained under the parent AFOSR grant, highly transparent Polycerams were obtained. The organic portions of these Polycerams were based on either polyethylene glycol with triethoxysilylpropyl-urethane and hydroxyl terminations (MPEOU) or hydroxyl-terminated polydimethylsiloxane (PDMS). These are shown schematically in Figure 4. Low molecular weight versions of these polymers were used in order to form low viscosity solutions suitable for dip coating.

Typically, Polycerams were formed with 80 vol% polymer and 20 vol% inorganic constituents. A processing procedure similar to that used by our group in converting Polyceram precursor solutions into high performance planar waveguides was employed. This procedure is outlined in Figure 5. The Polyceram solutions typically contained a solvent ratio expressed as moles of ethanol / moles of ($Ti + Si_{oxide} + Si_{polymer}$), with ratio values between 1 and 4. The solutions were formed in 100-1000 ml batches by initially mixing distilled ethanol, tetraethoxysilane (TEOS), and the functionalized polymer precursor (MPEOU or PDMS). Then acidified water was added and the solution refluxed to hydrolyze partially the alkoxide groups. In forming a titania-based Polyceram, titanium isopropoxide (TIP) was added in an additional step and the solution again refluxed. The ratio of the high index TiO_2 component to the SiO2 component directly alters the resulting refractive index of the final Polyceram. Solutions with Ti/Si ratios ranging from 2/1 to 0/1 were used for the

formation of GRIN lenses. After refluxing, the solutions were cooled to room temperature and stirred for 12-48 hours to promote condensation reactions and develop solutions with the range of viscosity needed for dip coating. The solutions were then stored in air-tight bottles at -25°C. The Polyceram solutions proved remarkably stable even at room temperature, provided they are stored in tightly closed containers and enough ethanol is present (e.g., an ethanol / (Ti+Si) alkoxide molar ratio of 2/1 or greater).

Polyceram Coatings on Glass Slides

The Polyceram solutions were characterized with respect to their coating and drying behavior. Solutions containing titania were observed to condense and dry many times faster than those synthesized without titania. This very likely reflects the catalytic effect of titania on silica condensation. In contrast, pure-silica solutions coated onto glass slides dried very slowly, remaining somewhat wet or tacky even after heating for 10 minutes at 120°C. The slow drying rate is due to the very slow condensation of silica, particularly under the acidic synthesis conditions used for homogenous Polyceram formation [4].

To study more closely the drying behavior of Polyceram coatings, a series of experiments were performed by coating glass slides in the coating machine. The thicknesses were measured using surface profilometry. In order to obtain reproducible measurements of coating thickness, a two-coat technique was developed. The use of two coatings allowed measurement of the thickness of a Polyceram coating on another Polyceram coating instead of measuring potential Polyceram/glass effects on the measured coating thickness. Thus, two coats were formed on the glass slide, with each coat separately dried. The second coat only overlapped half of the first coat, thereby providing a well defined step for the measurement of thickness.

Single Polyceram coatings could be formed with thicknesses of up to 20 μm without cracking -- in contrast to inorganic oxide gel coatings which are limited to a maximum thickness of about 0.5 μm if cracking during drying is to be avoided. Over a range of withdrawal speed, the thickness of the Polyceram coatings generally decreased linearly with increasing withdrawal speed. It was found, however, that minimum coating thicknesses were achieved at withdrawal speeds in the range of 1~2 mm/sec, as the thickness increased with further decreases in withdrawal speed. The relation between coating thickness and withdrawal speed for MPEOU - TiO_2-SiO_2 Polycerams formed from ethanolic solutions is shown in Figure 6.

The increase in thickness observed with decreasing withdrawal speed at very low speeds is due to solvent evaporation and gelation occurring more rapidly than the solution drains back into the solution bath. The coating thickness was largely independent of composition (i.e., the absence or presence of the titania component), but was strongly dependent upon the ethanol concentration. For example, by increasing the dilution of the Polyceram solution (i.e., the [EtOH] / [Ti + Si] ratio) from 2 to 4, the coating thickness became independent of withdrawal velocity except at very low velocities (see Figure 6).

Drying of the coated glass slides was carried out in the coating machine. Titania-containing solutions dried in less than 30 seconds, whereas pure silica solutions dried in approximately 3-10 minutes, depending upon the coating thickness. The effect of varying the Polyceram inorganic loadings from pure silica to 2:1 titania-silica was also investigated. Empirically, the addition of a very small amount of titania to the Polyceram was observed to reduce significantly the drying time of each coating layer. In general, with increasing titania content, the drying time was proportionately decreased. For example, a 1:1 molar TiO_2/SiO_2 Polyceram layer had a drying time halfway between that of the 2:1 and 0:1 (pure silica) layers.

In order to investigate the formation of a bulk material by a large number of serial coatings, multiple coatings were formed on glass slides. Following each individual coating step, the bulk material was heated in an oven located above the coating bath, similar to the single coating experiments. A large number of 2:1 titania-silica coatings could be formed without cracking or delamination of the Polyceram material from the glass slide. However, pure-silica solutions often formed a network of cracks after several days if not fully dried between the individual coating steps.

Cast Bulk Polycerams

Bulk monoliths were formed by gelling the Polyceram solutions in polyethylene vials. Monoliths were formed by initially covering 90% of the top surface of the vials to allow slow evaporation of the solvent. After enough solvent evaporates, the material uniformly gels with limited additional shrinkage of the material during further drying as compared to inorganic gels. After several days, the bulk piece may be handled and dried in air or in a vacuum oven to form a rigid material. Unfortunately, these bulk materials were often observed to craze or form large cracks when sectioned into smaller pieces -- particularly when exposed to water, alcohols, or acetone. Apparently, incomplete gelation and the entrapment of alcohol or water had occurred in the interior of the bulk material. By father allowing the bulk material to age for several weeks prior to sectioning, significant shrinkage and hardening of the bulk materials was observed. This reflected the increasing condensation and removal of solvent from the bulk material.

Bulk materials were also formed by pouring solutions into uncovered vials, thereby producing a greatly increased rate of solvent evaporation . In these samples, the Polyceram material formed a dry, dense skin on the exposed solution surface. This skin formation

effectively reduced further evaporation from the rest of the material. The thickness of the skin continued to increase with time; whereas beneath the skin, the fluid Polyceram solution remained.

Mixtures of Polyceram Solutions

Solutions corresponding to Polycerams of widely varied refractive index were mixed together to study if such solutions could be used to create a tailored solution which when dried would yield a Polyceram coating layer with customized refractive index. Based on research carried out under the parent AFOSR grant, increasing the amount of titania added to a silica-based Polyceram resulted in a linearly increasing refractive index. Thus, experiments were performed using pure silica Polyceram (low refractive index) and a 2:1 titania-silica Polyceram (high refractive index) solutions. The solutions, which were formed using the same synthesis process of Figure 5 were easily mixed together using a magnetic stirring plate and stir bar without causing precipitation or phase separation. Without initial stirring, however, the added solution tended to stay unmixed on top of the other solution. This suggests that the processing of the Polyceram solutions results in solutions without free water which would cause immediate condensation/precipitation of titania.

Dip Coating Machine for Forming GRIN Rods

In order to form bulk Polyceram rods which contain a large radial change in refractive index, a dip coating machine and coating technique were developed. The gradient in refractive index was achieved by varying the composition of the Polyceram coating bath between coating individual layers. Depending on the nature of the sample geometry, the dip

coating technique can be used to construct either cylindrical specimens with the gradient perpendicular to the cylinder axis, or planar-type samples with the gradient perpendicular to the plane.

In the present work, attention was focussed on developing cylindrical radial-GRIN (r-GRIN) lenses, which are the most desired GRIN lenses and the type for which the achievement of large diameter and large Δn has the greatest payoff. In the most common r-GRIN imaging form, the refractive index is highest at the center of the lens and parabolically decreases with increasing radial position. In order to form a refractive index gradient, two end-member Polyceram solutions were used. After drying , these solutions yield layers with quite different refractive indices. Initially the high refractive index solution is used in the coating bath and is gradually diluted over a number of coating cycles by the addition of the second, lower refractive index solution. Depending upon the volumes of high and low refractive index solutions used, the final refractive index of the layer deposited lies proportionately between the refractive indices of the two solutions.

The r-GRIN rod samples were formed using a computer-controlled coating machine developed to carry out, accurately and uniformly, a large number of coating operations while also making the necessary calculations and adjustments in the composition of the solution to form the desired refractive index gradient. A schematic diagram of the coating machine is given in Figure 7. An IBM-compatible personal computer has been used to time and control the coating process. The computer communicates via RS-232C serial interfaces to the various components of the coating machine and also records data during the coating process on an internal hard disk.

The computer is used to execute a BASIC program developed in-house for the dip coating process. Initially, the program reads-in an appropriate data file which contains information including the length and diameter of the rods desired, the type of GRIN profile desired, the

drying time between coatings, the volumes and refractive indices of the Polyceram solutions to be used, the withdrawal velocity, and solution viscosity. Using these data, the coating program makes the necessary calculations to construct the desired gradient profile. Then, the computer commences the coating process by controlling the drive motor, pump, and other peripheral equipment.

The computer directly controls a very precise stepper motor drive and extension cylinder which lower and raise the sample into and out of the solution bath. The computer controls the exact number of turns that the stepper motor makes, with a resolution of 128 steps / motor revolution. The cylinder attached to the stepper motor has an extension of 30 cm, and can be positioned within a micron due to the high resolution of the motor. The cylinder is mounted vertically inside the coating machine.

A programmable pump is also interfaced to the computer, which is used to add the secondary solution to the primary solution bath. The pump system also contains a stepper motor and can control the amount of solution pumped to within a accuracy of better than $\pm$ 1% of the desired volume. Further, two relays are interfaced to the computer to control rotation of the sample during drying, and to allow stirring of the solution bath after a new portion of solution is added.

The oven used for drying each individual coating layer was formed using a heating tape wrapped around a four inch diameter quartz tube. The heating tape was controlled by a variable transformer and calibrated periodically with a thermocouple placed inside the quartz tube. The convection air currents created by the oven were found to impede significantly the ability to dry the Polyceram sample. To counter the effects of the convection bottom of the tube was closed off by securing it to the top of the solution bath (see Figure 7 or Figure 8), thereby creating an effectively stagnant air space inside the tube, particularly below the

furnace. This created a much improved drying process and also lowered the evaporation rate of the solution bath, which was previously exposed to the ambient atmosphere.

The Polyceram solution bath consists of a large aluminum cylinder with copper cooling coils around the outside. At the center of the cylinder is an opening for a 80 ml polyethylene vial which is initially filled with 40 ml of the high refractive index solution and a magnetic stir bar. During the coating process, the vial is gradually diluted with low refractive index solution. Due to the formation of the GRIN sample and solvent evaporation, approximately 10-15% of the entire solution is removed from the solution bath. The solution bath was initially chilled to 15°C for the purpose of reducing the evaporation of solvent. It was found, however, that cooling of the solution increased unduly the thickness of the undivided coating layers due to the increased solution viscosity. Thus, the cooling of the solution bath was discontinued and coating was performed at room temperature.

Summary

During the first year, pure-silica and 2:1 molar titania:silica MPEOU- and PDMS-based Polyceram solutions were used to form bulk Polyceram materials by a dip-coating technique. A computer-controlled coating apparatus was constructed for the formation of highly accurate coatings of changing composition. Monolithic bulk Polyceram samples were formed by multiple coating cycles. The effects of solution concentration (ethanol / inorganic ratio), and drying time/temperature per individual coating layers were examined. Typical coatings were 5-15 microns thick, which proved difficult to dry, for SiO_2 -rich compositions.

VII. YEAR 2 RESEARCH (1993-1994)

Improvements in the Coating Machine

A number of improvements were performed on the coating machine. First, an electronic furnace controller was installed in order to provide improved temperature stability for the drying process. The former use of a variable transformer allowed the temperature of the drying process to vary by +/- 10 degrees; and it proved difficult to return to a set temperature after changing the temperature. Further, the new furnace controller came equipped with an RS-232C interface, which allows systematic variation of the drying temperature in addition to the drying time as currently used. This feature will be implemented as part of ongoing research.

Secondly, the coating apparatus was fully enclosed and tightly sealed to reduce and stabilize the humidity within the apparatus. A digital hygrometer installed in the coating chamber indicated that a very low ~10% relative humidity or less was maintained in the chamber. Further, due to the drying effect of the oven over the solution bath, the relative humidity in the drying portion of the coating machine was maintained at $\leq 2\%$, which was the lowest reading of the hygrometer. Thus, the closed quartz tube, open at the top, effectively removed humidity from the solution bath and provided a consistent and reproducible coating atmosphere.

The GRIN Coating Process

The formation of a cylindrical Polyceram r-GRIN sample rod requires that a bait rod or fiber be used to form the center of the rod. In the initial development of the process, we used 1 mm diameter glass capillary tubes, sealed at the bottom. The glass capillary is placed in

a chuck assembly which is attached to the cylinder arm. A motor at the top of the chuck assembly can rotate the sample in order to heat uniformly the sample within the oven between framing the individual coating layers.

When activated, the computer executes the appropriate number of cycles to form the GRIN material. A typical coating cycle consists of seven steps, as shown schematically in Figure 8. Initially, the samples is lowered and dipped into the solution bath. Then, the sample is withdrawn and raised up into an oven to dry the individual coating layer. Immediately after the sample is withdrawn, a portion of the low refractive index solution is added to the solution bath and magnetically stirred for 30 seconds. During drying, the sample is slowly rotated at 3 rpm to dry evenly the deposited layer at temperature typically in the range of ~100°C for PDMS-based Polycerams and 120-130°C for MPEOU-based Polycerams. The drying times typically varied from 15-45 seconds for 2:1 titania:silica coatings up to 150-300 seconds for a nearly pure silica-based Polyceram layers - both sets of values being applicable for coating thicknesses in the range of 2-10 μm. The sample is repetitively coated until the desired index profile and diameter is obtained. An additional small number of coats are added to provide a cladding for the lens rod.

A number of GRIN samples and monolithic samples were formed during the second year using both the original and modified coating machine. The formation of monolithic samples using the end-member (high and low refractive index) solutions provided valuable information on the appropriate drying times and coating thicknesses formed. GRIN samples were formed containing either a linear or parabolic gradient, decreasing from the high index halfway to the low index value. The pure-silica samples were very clear, whereas the titania-silica samples were clear but lightly yellow in color due to the characteristic adsorption of reduced titania. A fraction of the samples during the first two years formed cracks either during the coating process or within several days of the completion of coating. Typically,

cracks were formed at the top of the sample and traveled in a spiral pattern down through the sample. The typically coating thicknesses for these samples were 5-12 μm, using solvent ratios from 1.7 to 2. The thicknesses obtained by dip coating the glass capillaries were always about double the thickness of equivalent coatings formed on glass slides.

Post-Treatment / Polishing

During the first year, only a few dip-coated Polyceram materials were characterized for uniformity and thickness of the coatings. This was primarily due to difficulties in creating samples which remained uncracked during the coating and subsequent drying and polishing processes. After formation, the GRIN samples were sectioned perpendicular to the gradient using a diamond saw and either oil, water, or no lubricant. It was found that most samples cracked within minutes of sectioning, due to incomplete drying of the interior material. Many of the samples which exhibited a large degree of cracking were found to smell of ethanol. Further, the cross-sectional surfaces of many samples were observed to swell when initially exposed to water, and subsequently formed cracks resulting from exposure to the water.

In order to improve the stability of the GRIN samples, most were further heated either in a conventional air oven or vacuum oven at 50-120°C for 5-30 days to obtain further condensation in the material. At temperatures above 100°C, the MPEOU-based Polycerams became increasingly opaque and bubbles were occasionally formed in the interior of samples heated in the vacuum oven. Samples containing the MPEOU polymer were very stiff and brittle when dried, whereas the PDMS-based samples retained a fair degree of flexibility after drying. The net effect of the additional drying step was that samples were more rigid and brittle; and a sizable majority of the samples formed catastrophic cracks during the drying step.

A modified polishing method was therefore developed for the bulk Polyceram materials. After sectioning, the samples were placed into molds and covered with an epoxy resin which cured in 12-18 hours. A number (6-10) of the epoxy mounts could be then polished simultaneously using automated polishing equipment. The preferred polish recipe consisted of an initial grinding step using 600 grit silicon carbide paper with water as a lubricant. Then (a) a 6 micron water-based diamond suspension; (b) a 0.3 micron alumina slurry; and © a 0.06 micron alumina slurry were used in sequence. In between steps, the samples were washed with water and placed in an ultrasonic bath to remove the previous abrasive material. Only 25 minutes were required to polish a collection of samples.

As the drying time per coating was appropriately increased, samples were only infrequently observed to crack during the coating process or during the sectioning process. Increasingly, the use of water, ethanol, and acetone during the polishing process did not appear affect the appearance or mechanical properties of the Polyceram GRIN materials.

Polyceram Fibers

In order to form effective Polyceram GRIN lenses, the glass capillary tubes and glass fibers initially used as a bait rod were changed to Polyceram fibers. Fibers were formed by drawing in a similar manner as that used to form inorganic sol-gel fibers [29]. A 20-40 ml volume of solution was added to an 80 ml polyethylene vial and allowed to age and thicken (with the vial uncovered) as a portion of the solvent evaporates over 5-7 days. Eventually, the viscosity of the solution increases to the point where a fiber can be drawn. Typical fibers wee 20-100 microns in diameter. By covering the vial and adding 3-5 drops of ethanol, larger diameter fibers could be drawn 12 hours later with diameters of 200-500 microns. Examination of the fibers in the optical microscope indicated that the fibers were very uniform and cylindrical.

After fiber formation, the fibers were cut into 5 cm lengths. Some of the fibers were either heated/cured in a vacuum oven at 100-130 C for 1 hour, or heated in a microwave oven at 30% power for 5 hours. A 0.5 cm length of the fiber is then attached to a 5 cm length of glass capillary rod using super glue. The glass rod is provided to hold the fiber properly in the drill chuck located at the end of the extension arm. The fibers formed are sufficiently strong that they are fully capable of supporting the weight of the coating sample, although the adhesive used to attach the fiber to the glass rod was observed to embrittle somewhat the fiber at the point of attachment.

During the initial portion of the coating process, the fiber is initially lowered into the solution bath and allowed to soak for 10 minutes. This allows swelling of the fiber to occur, thereby enhancing the uniformity of the initial coating layer on the fiber--as well as minimizing the possibility of forming a sharp interface between the fiber and subsequent coating layers. Unfortunately, examination of the interface using optical microscopy indicated that a circular crack often formed between the fiber and the first coating layer in

many of the samples. It was found that this occurred more frequently for fibers which were not initially cured, or in circumstances when the coating were not adequately dried between forming individual coating layers.

The samples in which the circular interface cracks were observed also typically formed 3-10 additional cracks radiating outward from the interface. It is believed that the formation of the circular interface cracks was due to weak bonding and shrinkage which occurs at the interface. These cracks only occurred during sectioning, not during the coating process. Similarly, the occurrence of radial cracking was observed to form approximately 12-100 hours after sectioning or polishing of the material, presumably from flaws or damage formed after cracking occurs at the fiber first coating layer interface.

Sample Preparation for SEM or Optical Characterization of the GRIN Profile

Samples approximately 1 mm thick were prepared by sectioning and polishing both sides of the Polyceram GRIN material. The primary reason for the formation of the thin samples was for characterization by Mach-Zender interferometry, which yields information about the uniformity and distribution of the refractive index gradient in the material. For the Mach-Zender technique, a laser is transmitted through the material and the path difference with a reference beam is measured at a detector. This path difference is related to the variation in the refractive index. The technique yields two-dimensional contour plots of the refractive index profile consisting of light and dark fringes (in the present case in the form of circular rings due to the radial refractive index gradient).

Typically, 6-10 thin Polyceram samples (in epoxy mounts) were attached to a metal platen for polishing. Only a portion of the epoxy mount was glued to avoid any contact with the GRIN material. After polishing one side, the samples were gently removed from the

platen and the second side glued down and polished. The remaining glue on the opposite side was dissolved by placing the samples in an acetone-filled sonic bath for several minutes.

SEM Characterization of the Polyceram Composition and GRIN Profile

Thin GRIN and monolithic Polyceram samples were sectioned and then examined in the scanning electron microscope to obtain information on the morphology and composition of the Polyceram material. Examination of the materials within the microscope indicated no sharp interfaces between the individual coating layers or between the fiber core and the initial coatings. Initially, small bubbles or pores were observed in circular arcs--apparently at interfaces between coatings. As the per-layer drying time was increased, the pores substantially disappeared due to more complete drying.

The SEM had a electron dispersive spectrometer (EDS) probe which was used to collect quantitative information on the composition of the GRIN material. The approximate interaction volume sampled by the probe was about a micron in diameter and width, but varied slightly with the accelerating voltage and current used in the SEM. Compositional analyses were taken at uniform distances from the center to the edge of the lenses to determine the proportions of titanium to silicon. Carbon, oxygen, and hydrogen could not be detected due to their low atomic numbers). By plotting the Ti/Si ratio as a function of radius, the refractive index profile could be quickly determined.

Summary

A number of improvements were made to the coating apparatus which significantly improved the formation of bulk Polyceram GRIN materials by the multiple dip coating technique, including improved oven control and enclosing of the Polyceram solution bath. The primary measure of improvement was the significant decrease in the amount of catastrophic cracking and shrinkage of the Polyceram GRIN materials--particularly due to improved per-coat drying and subsequent microwave drying. The use of Polyceram fibers significantly improved the uniformity and quality of the coatings, despite the occasional formation of interfacial cracking at the fiber/initial coat interface. The ability to section and polish the GRIN samples allowed the examination of the materials in the SEM and the determination of refractive index profiles.

VIII. YEAR 3 RESEARCH (1994-1995)

Coating Machine Improvements

Further improvements to the Polyceram dip coating machine were made to eliminate machine vibrations which were observed to affect adversely the formation of uniform coating layers. The primary source of vibration was the stepper motor, particularly during acceleration and deceleration of the sample rod. The effect of the vibration during acceleration out of the solution bath was to form wavy coating layers, which are unacceptable for the formation of optical-quality lens rods. A large fraction of the stepper motor-associated vibration was eliminated by redesigning the motion transfer from the motor's extension cylinder to the sample fixture. Although initially connected together, the two parts were separated, and a set of pulleys and cables were installed between them. Although the initial portion of the metal cable vibrates with most of the vibration of the motor, after passing over two pulleys, nearly all of the vibration is dissipated.

Viscosity Measurements

Work was performed to measure the room temperature viscosity of the Polyceram solutions using a digital Brookfield viscometer. Initially, the viscosity experiments were designed to simulate and determine the increase in viscosity of the solution bath used in the coating system. Because the solution bath can be regarded as an open vial, a portion of the ethanol solvent evaporates during the coating process, thereby increasing the viscosity of the solution. A small sample adapter was attached to the viscometer, which held 8 ml of the Polyceram solution instead of the 300-500 ml of solution contained in a larger beaker as traditionally used for viscosity measurements. Unfortunately, the small sample volume was observed to form a surface skin on the solution after about 15 minutes due to the evaporation

of the solvent from the solution. After the skin was formed, the viscosity readings were erratic as the rotating spindle would adhere to and break free of the coating while rotating. To reduce this effect, experiments were also performed by substantially covering the solution to minimize evaporation.

Measurements were also performed to monitor the increase in viscosity (aging behavior) of solutions stored in closed vials at room temperature and at -25 C. Polyceram solutions with an [EtOH]/[Ti + Si] ratio of 2 had initial viscosities of 7-8 centipoise. Both the samples stored at room temperature and at -25 C had the same viscosity when portions of the solutions were measured at room temperature. The viscosity changes very slowly, increasing to only 10-11 centipoise within a month. Hence there was considerable shelf life of the coating solutions. There was no significant viscosity difference between the pure silica and 2:1 titania-silica Polyceram solutions, as the viscosity is primarily controlled by the larger polymer molecules.

Change of Polyceram Solvent

It was believed that a significant impediment to the efficient formation of bulk GRIN lens devices was the relatively large amount of ethanol retained within the bulk of the Polyceram material. For this reason, a number of solvents with higher vapor pressures were studied to determine their suitability for partially or totally replacing the ethanol. Particularly attractive results were obtained using a solvent with which we had extensive previous experience under the parent AFOSR grant in the synthesis of Polycerams - viz. tetrahydrofuran (THF). The use of this solvent was highly successful in both partial and total substitution for ethanol. Effectively, the use of THF allowed the Polyceram coatings as well as bulk cast materials to dry faster than equivalent ethanol-based Polycerams.

Microwave Curing

A conventional 800 watt microwave oven was used to cure the materials after dip coating, similar to the use of the vacuum oven. The microwave power, provided operating at 2.45 GHz, excites the OH bonds present in the Polyceram coating layers. Such bonds are found as free water and silanol groups, as well as in retained ethanol. In drying the Polyceram materials in this way, samples were rotated and heated using 10-30% of full oven power. As an example, at 10% power, the sample is heated for a total of 6 seconds per minute. Typical complete Polyceram GRIN samples were heated in the microwave oven for 5-30 hours. Drying times were limited to approximately 30 hours, since after such a period the samples were observed to darken slightly in color, due to degradation of the polymer or reduction of the titania species present. The GRIN samples typically were crack-free or exhibited significantly reduced cracking behavior as a result of microwave drying compared with the use of conventional air-drawn ovens or vacuum ovens.

Surfactants

The effect of adding a surfactant to the coating process was investigated. A polyethylene glycol-based surfactant (Triton X-100) was commonly added to the initial Polyceram solutions in amounts ranging from 0.05 to 1 weight percent. Comparisons among samples formed with and without surfactant indicated very little improvement in the coating uniformity or the thickness of the coating layers formed. Similarly, the drying of Polyceram materials containing a surfactant appeared no different than materials without surfactant.

General Findings

By the end of the third year of the AASERT project, it was demonstrated that large diameter (> 25 mm) r-GRIN rods and monolithics can be formed by a dip coating process using a computer controlled dip coater and oven developed during the project. Coating layers with tailored thickness and refractive index could be precisely formed using the computer control. Further, very thick coatings (up to 20 microns) could be easily formed using the same dip coating process. In addition, bulk monolithic materials could be formed by casting and slowly drying the Polyceram materials.

It was found that Polyceram materials provide the necessary flexibility during the drying stage, thereby allowing very thick coatings to be formed. Unlike sol-gel derived oxide coatings, the polymer components of Polyceram materials contributes increased flexibility in drying as well as initial solution stability. The polymer components also provide dip coating uniformity for many coatings -- including improved coating characteristics over numerous coating cycles. Unlike sol-gel oxide coatings which contain significant porosity, the nature of the Polyceram materials results in an absence of detectable porosity in the dried gels, even for gels synthesized with small solids contents. To avoid entrapment of the solvent or of the water formed during the condensation (curing) reactions in processing Polycerams materials, we have discovered that the thorough drying of individual coating layers results in greatly improved long-term mechanical stability of the final materials, due to a greater extent of condensation and removal of solvents under conditions where the Polycerams are relatively flexible.

Most work carried out to date has focussed on Polycerams containing relatively high volume fractions of polymer (typically in the range of 60-80%). Recent work has initiated investigation of Polycerams containing smaller polymer contents (in the range of 5-50%) in order to facilitate solvent removal during drying of the individual coating layers. Preliminary

results indicate that even the smaller polymer contents are sufficient to avoid cracking of the layers associated with drying stresses.

The silica-titania system used in the present research program is a very well behaved system for the synthesis of GRIN Polyceram materials. Synthesis of the initial Polyceram solutions as well as the stability of the solutions once formed, were very good. The ability which has been demonstrated to mix different Polyceram solutions with considerably different states of hydrolysis and condensation as well as with notable disparity in the condensation rates suggests that the formation of Polyceram composite polymers within the solutions has a very significant effect in preventing possible phase separation or precipitation when mixed.

Finally, there appears to be a significant and beneficial effect of using microwave drying to heat selectively residual water, hydroxyl, and alcohol groups in the formed Polyceram rods. This form of heating is quite localized and appears to be highly efficient in producing dense, hard, highly stable Polyceram GRIN materials.

IX. CONCLUSIONS/ACCOMPLISHMENTS

The accomplishments of the current research program include the following:

(1) It has been demonstrated that Polycerams are excellent materials for the formation of highly transparent (low attenuation) optical materials which contain a large gradient refractive index;

(2) It has only demonstrated that bulk Polyceram GRIN materials containing either cylindrical or axial gradients in refractive index can be formed using a repetitive dip coating approach to forming individual layers with different refractive indices.

(3) It has been demonstrated that the refractive index profile - and potentially the profile of other properties of the Polycerams - can be easily tailored by the mixing specified concentrations of two highly disparate Polyceram solutions prior to depositing individual layers.

(4) The improved drying capability of Polcerams as compared to oxide coatings has allowed the rapid formation of single coatings with thicknesses of 20 microns or more (compared with about 0.5 micron for oxide coatings). It was found to be important that individual coating layers be dried extensively before depositing subsequent layers. This reflects the fact that Polyceram materials are highly dense and can retain significant solvent and water.

(5) The use of a computer controlled dip coating system coupled with measured refractive index vs. composition relations enabled the formation of high quality rods with tailored radial variations in refractive index.

(6) Effective vibratrion isolation of the coating bath from the motor used to effect dipping is important in obtaining high quality materials.

(7) Microwave drying of the formed Polyceram rods is an important final step in obtaining dense, solvent-free bodies.

(8) Overall, the ability to produce large diameter rods with tailored radial gradient in refractive index depends on the effective integration of precursor chemistry, synthesis conditions, layer deposition and drying, and overall removal of solvent from the final formed bodies.

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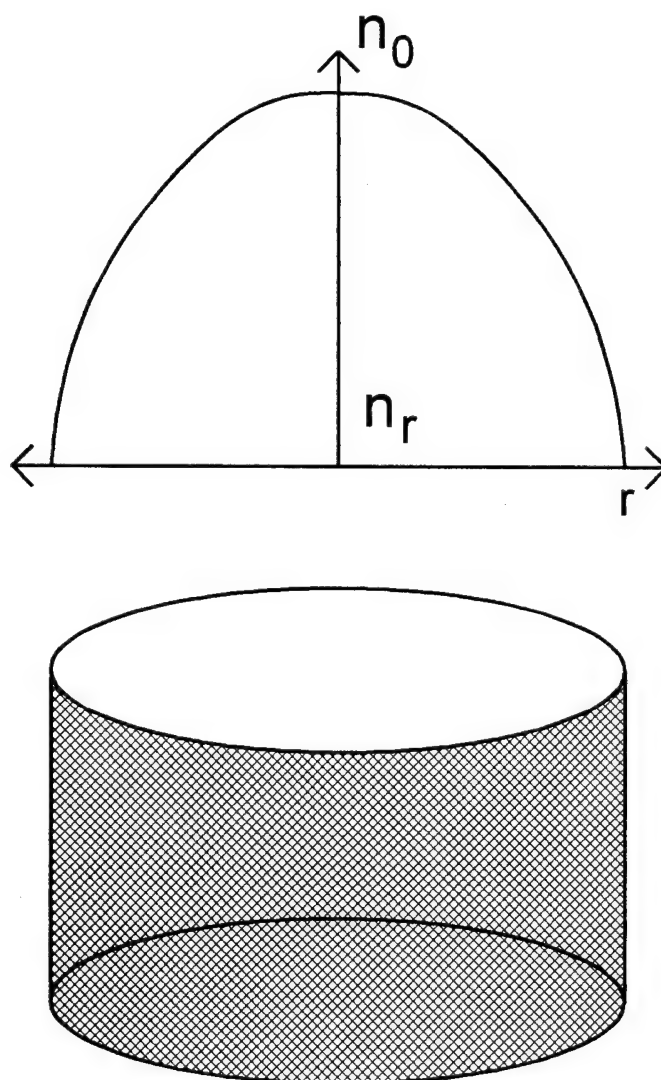31. Sakai in MRS Symp. Proc. Vol. 32 (1984) 91-99

Cylindrical r-GRIN lens

Figure 1. Cylindrical r-GRIN lens and typical parabolic refractive index profile.

Convex Cylindrical
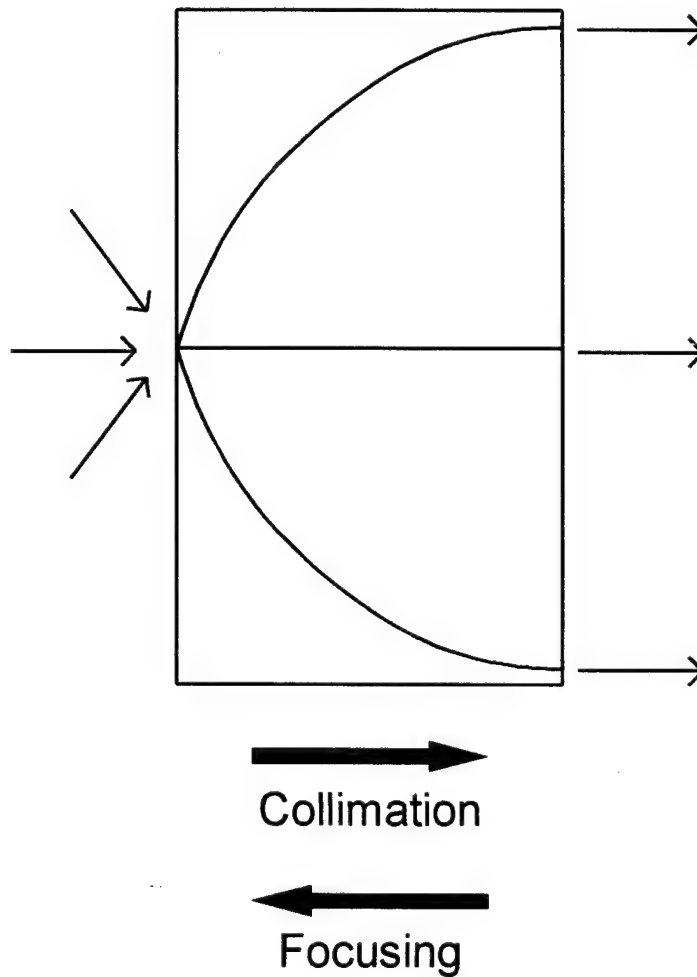# GRIN Lens

Collimation

Focusing

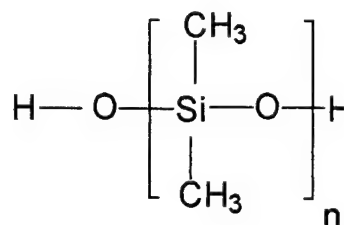**Figure 2.** Side view of a r-GRIN lens showing ability to focus or collimate an image.

Convex Cylindrical
GRIN Lens

Magnificaton
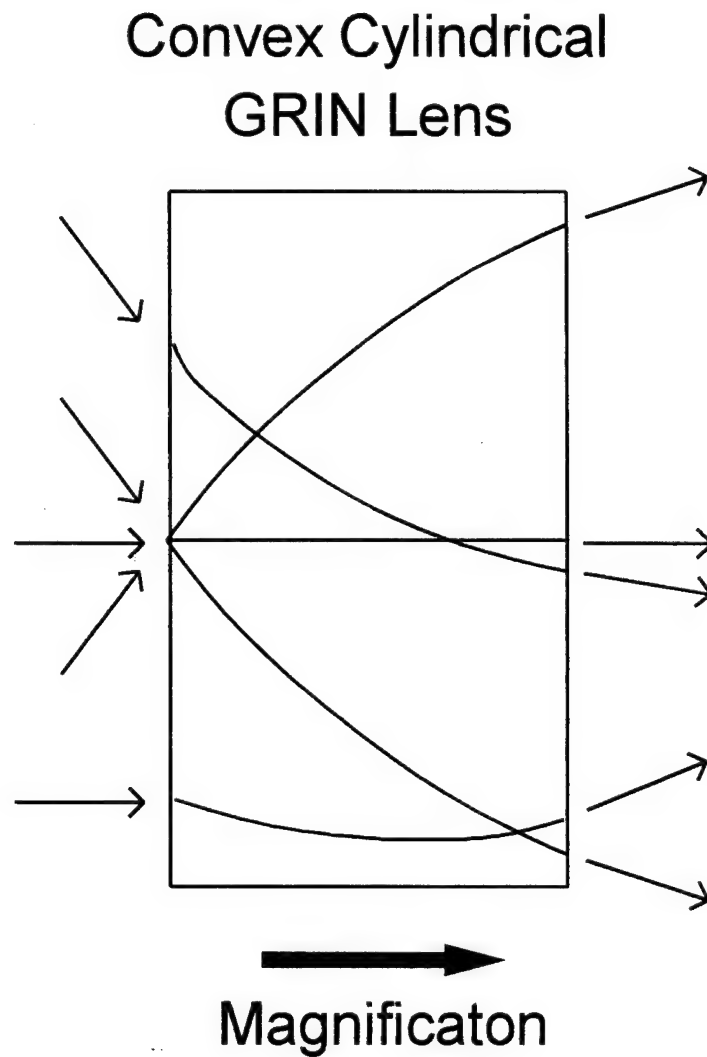
Figure 3. Side view of r-GRIN lens ability to magnify an image.

MPEOU
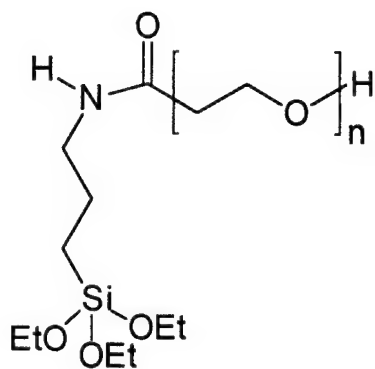
PDMS

Molecular weight ~ 300-400
PEO units ~ 4

Molecular weight ~ 410
DMS units ~ 6 - 7

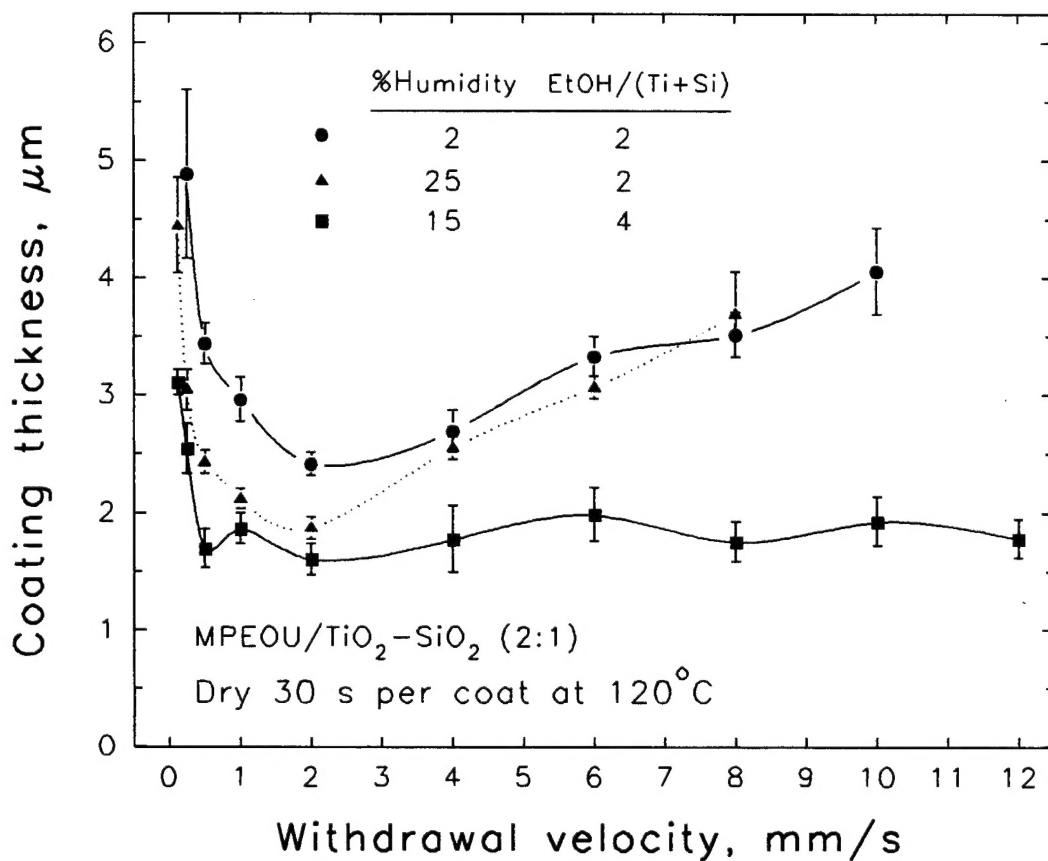**Figure 4**. Structures of polymers used in the synthesis of GRIN Polycerams.

Figure 5. A graph of MPEOU/TiO$_2$-SiO$_2$ coating thickness versus withdrawal velocity with several values of humidity and EtOH/(Ti+Si) ratio.
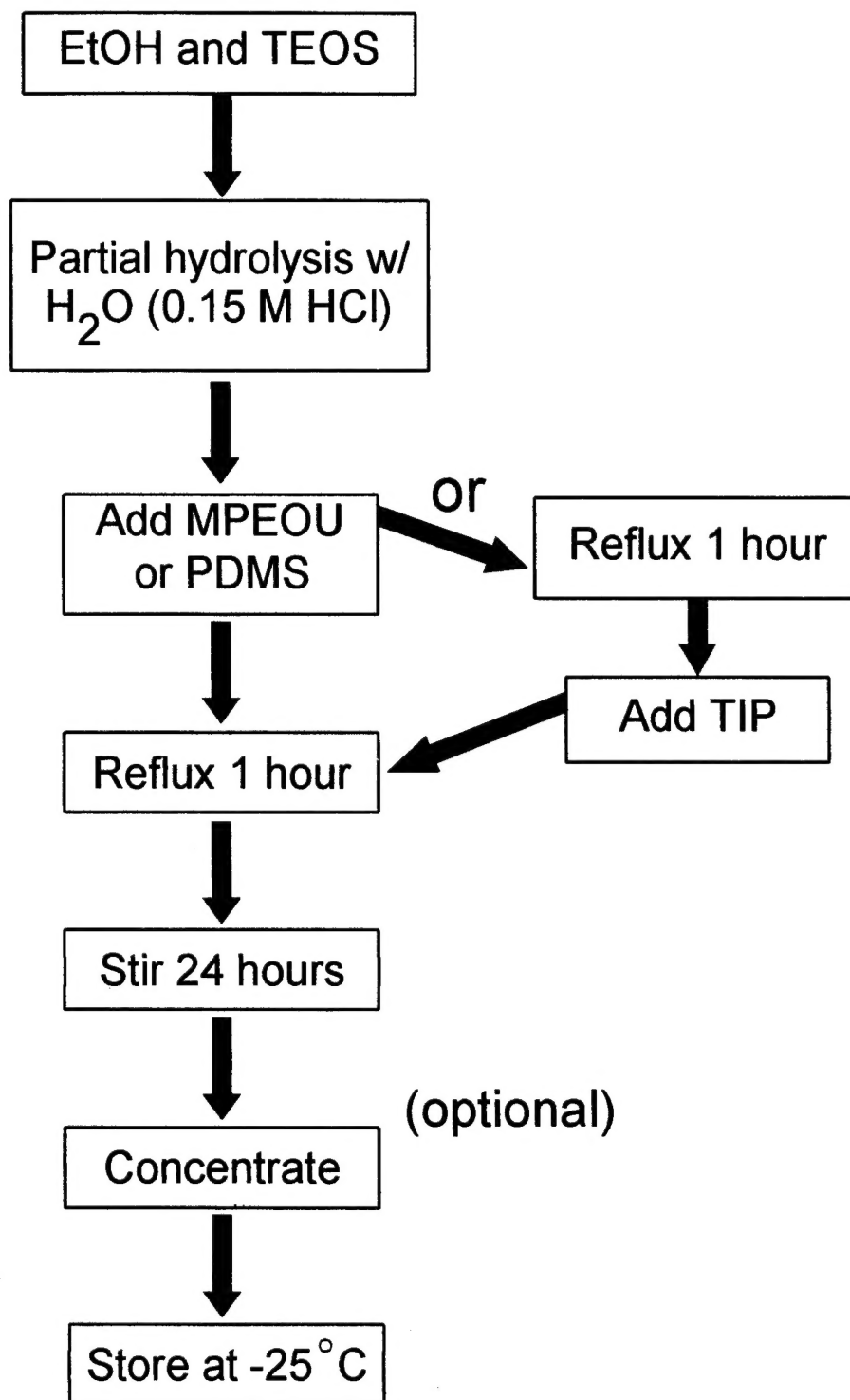
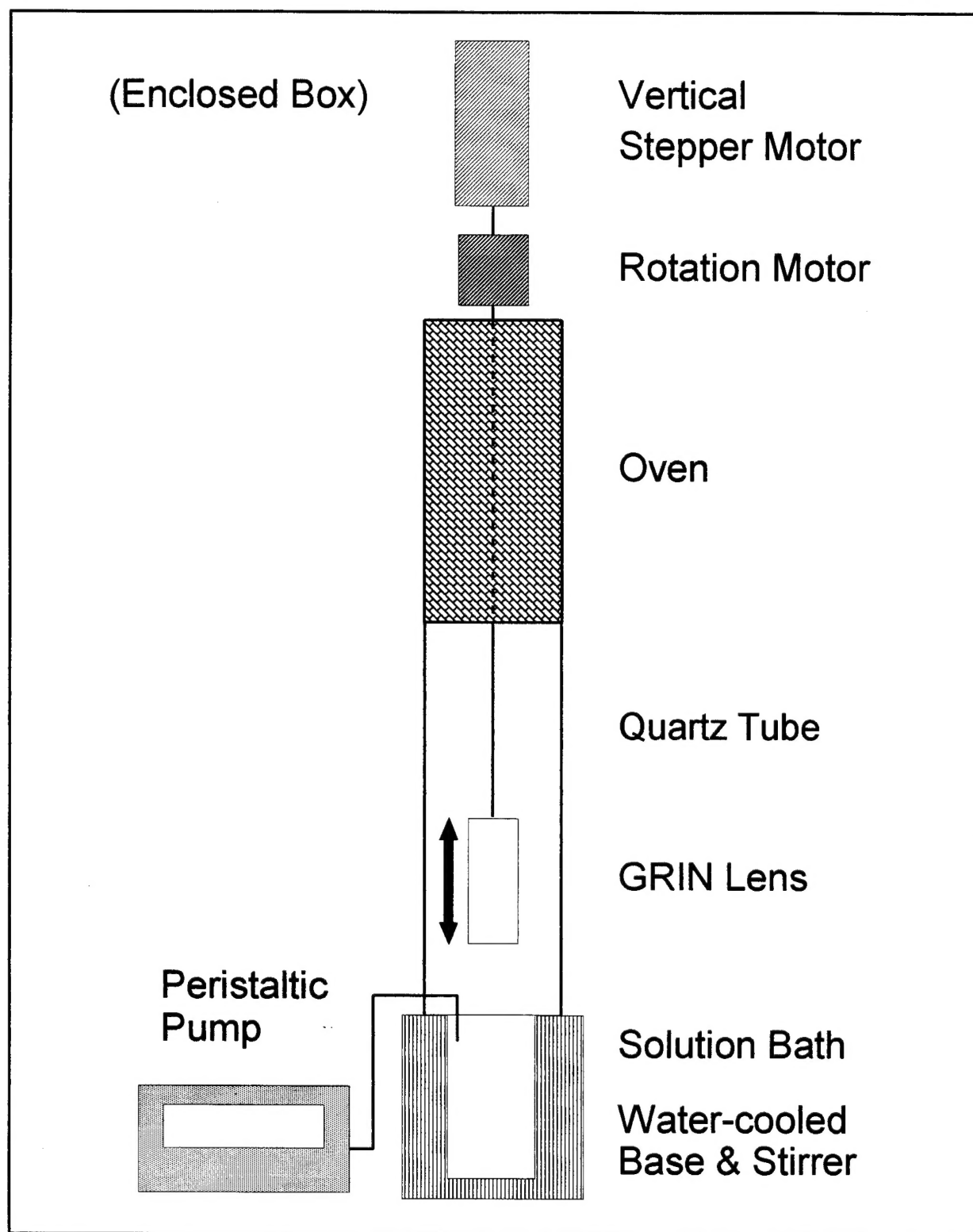**Figure 6**. Flow chart for the synthesis of Polyceram GRIN solutions.

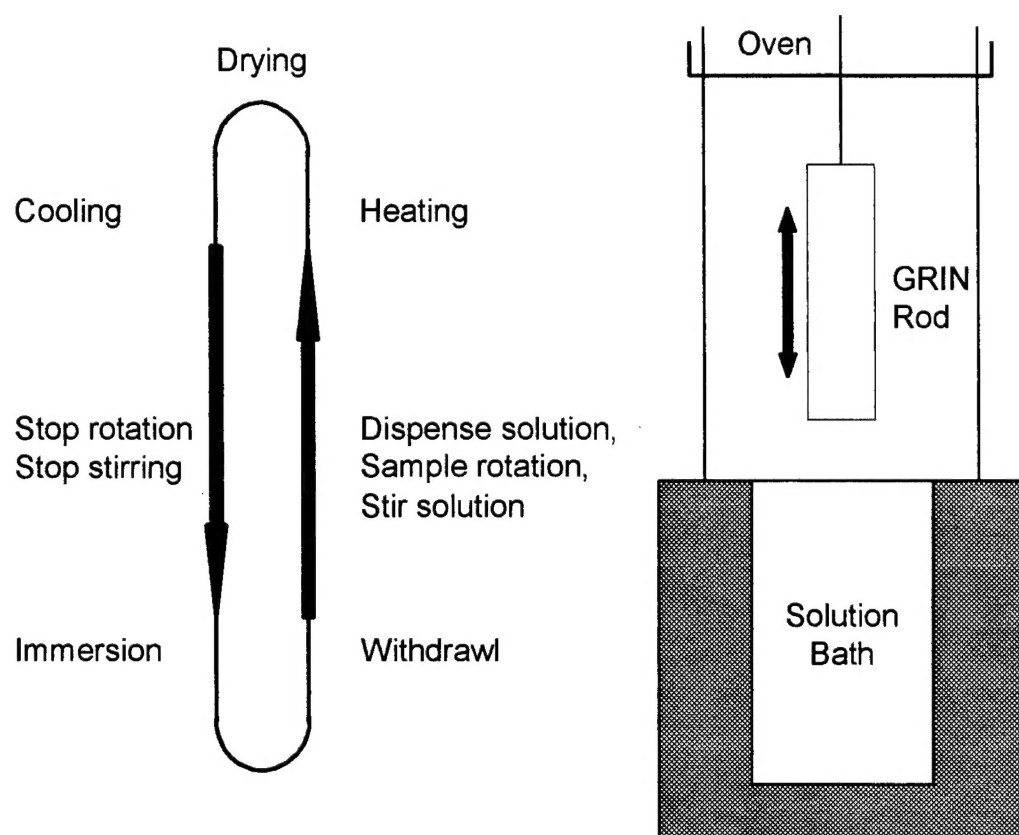**Figure 7.** Schematic of GRIN coating machine.

Figure 8. Flow diagram indicating the 7 separate steps performed each coating cycle.